

Iron–phosphorus–carbon system

Part 3 – Metallography of low carbon iron–phosphorus alloys

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Metallographic examination of archeological phosphoric iron and specially prepared iron–phosphorus alloys sometimes reveals unusual ‘ghosting’ features within ferrite grains when nital is used as an etch. The ghostlines mark the boundaries in phosphorus content arising from the dual phase ferrite–austenite microstructure, which existed at elevated temperatures. Nital preferentially attacks iron with lower phosphorus content, so giving a surface relief that characterises the phosphorus. Both ferrite–austenite and austenite–ferrite transformations occur by nucleation and growth, and also are accompanied by the diffusion of phosphorus. The morphologies of phases formed conform to the Dubé classification system. The microstructures observed in archeological irons are consistent with those produced by the ferrite–austenite transformation. Hence, understanding of the microstructures produced in this current work allows fuller interpretation of the microstructures found in archeological artefacts. **MST/4404**

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Introduction

Phosphoric iron, containing typically 0.05–0.5 wt-%P and less than 0.1 wt-%C, is found relatively frequently in bloomery iron artefacts.¹ Metallographic examination of a phosphoric iron, etched with nital, sometimes produces a watery shimmer or wrinkled appearance in the ferrite grains.² This ‘ghosting’ is visible as a slight contrast against the background of the ferrite grains. The effect is usually indistinct and irregular although the ferrite grain structure and any carbides present etch clearly. Occasionally, however, this ghosting is sharply defined with distinct boundaries or shows a degree of order, both of which suggest that it may be produced by a metallurgical phase transformation.^{1,2}

Stead³ described a feature observed in steels where local segregation of phosphorus produced regions which were fully ferritic and distinctly visible in a pearlitic matrix. His ‘ghost lines’ were produced by the same mechanism as that responsible for the formation of banding in steels, i.e. where solute segregation locally changes the onset of ferrite formation during cooling from the austenitic regime.⁴ Despite being referred to by the same term, the ghosting investigated here is an entirely different phenomenon, occurring within grains of ferrite, and not as contrast between pearlite and carbide free regions.

The phosphorus contents of archeological phosphoric irons are too low for the precipitation of phosphide to have occurred and so the ghosting cannot be the product of phosphide precipitation.^{5,6} However, if an iron–phosphorus alloy which has been quenched from the dual phase ferrite–austenite region is etched with nital, distinct boundaries are visible at prior phase interfaces, and these are attributed to sharp changes in phosphorus content.⁷ Metallographic analysis of archeological artefacts reveals that the lines of the ghosting patterns correspond to local changes in phosphorus content. Figures 1 and 2 show examples from two different knives. Fig. 1d shows an allotriomorphic structure with secondary side plates (cf. Fig. 4).

Macroscopic segregation of phosphorus results from inhomogeneity of the original bloom and subsequent

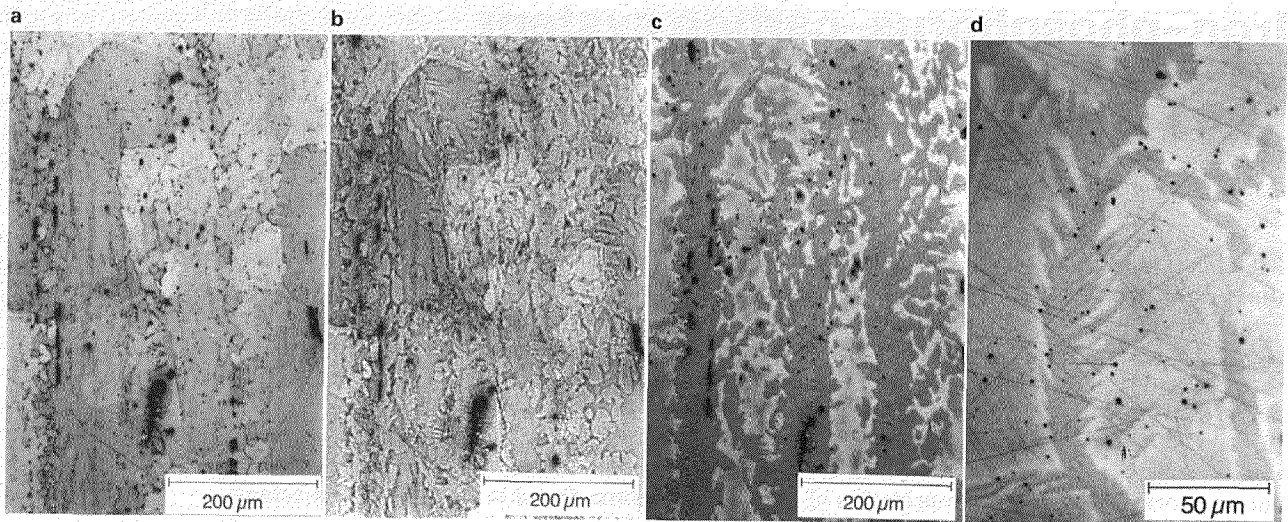
oxidation and interdiffusion effects during forging. However, the microstructural phosphorus segregation which has been observed in archeological iron using Oberhoffer’s reagent is consistent with that produced by the diffusional growth of austenite in a ferritic matrix.⁴ As the rate of diffusion of phosphorus in austenite is less than in ferrite, the kinetics of the diffusion controlled austenite–ferrite reaction in the dual phase region is slow relative to the reverse reaction.⁷ Thus, the growth of ferrite from an austenitic matrix is limited by the diffusion of phosphorus into the austenitic bulk.

It is unlikely that, when forging a piece of phosphoric iron on a charcoal hearth, a heat treatment could have been given which would have austenitised the iron and then held it in the narrow dual phase range for sufficient time for full precipitation of ferrite from austenite to occur accompanied by the diffusion of phosphorus. Once the temperature of the piece fell below the dual phase range, any remaining austenite would have transformed rapidly by a massive transformation.⁸ However, the investigation of the austenite–ferrite transformation remains of interest as part of this study. First it allows observation of the phosphorus microsegregation remaining from the transformation at high temperature permitting comparison with the patterns visible in preindustrial iron artefacts. Second, the morphologies of the ferrite produced can be investigated, as can the extent to which phosphorus is partitioned during the transformation. This second aim is primarily of metallurgical rather than archeometallurgical interest.

Accordingly, in order that the ghosting microstructures observed in phosphoric iron can be explained fully, it is important to understand how dual phase microstructures develop and also how they respond to nital.

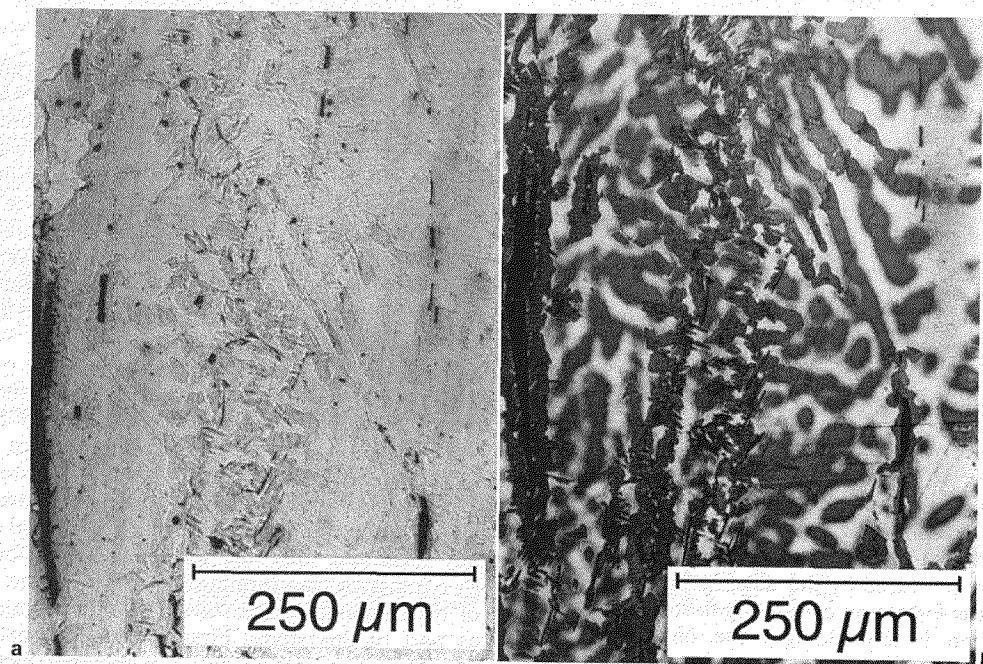
Previous metallographic studies of iron–phosphorus alloys

Haughton⁹ quenched a series of iron–phosphorus alloys after annealing at temperatures in the range 900–1050°C. He attempted to determine the boundaries of the dual phase loop by metallographic examination of the quenched



a etched with nital, in focus; b etched with nital, out of focus to show ghosting; c etched with Oberhoffer's reagent; d prior austenite allotriomorphs with secondary side plates in another region of same knife, etched with Oberhoffer's reagent

- 1 Detail from microstructure of Anglo-Saxon knife showing banding in ferrite grain size and ghosting: found during excavation of late pagan, Anglo-Saxon cemetery dating from late sixth or early seventh century AD; black regions are non-metallic inclusions; Oberhoffer's reagent deposits copper preferentially on areas of lower phosphorus content, giving darker regions that were low phosphorus austenite and lighter regions that were higher phosphorus prior ferrite



a etched with nital; b etched with Oberhoffer's reagent

- 2 Detail from back of Anglo-Saxon knife showing ghosting remnant from prior phase microstructure: knife found during excavation of late pagan, Anglo-Saxon cemetery dating from the late sixth or early seventh century AD; black regions are non-metallic inclusions

specimens and showed several photographs of microstructures, which showed that two phases had been present at elevated temperature.

Vogel¹⁰ also determined the iron-phosphorus phase diagram by experimenting with a series of iron-phosphorus alloys (although he did not specify their purity) and by examining the microstructures that could be produced by quenching rapidly from the dual phase field. He found that microstructures, which showed evidence of partial transformation to austenite, could be produced in iron-phosphorus alloys containing less than 0.6 wt-%P. Etching with nital revealed the phase boundaries which existed at elevated temperature. A short heat treatment in the dual phase range resulted in the formation of needles of austenite

and heating at a higher temperature promoted spheroidisation of the austenite needles, the driving force being the reduction in the surface area between the ferrite and austenite phases. A slower cooling rate resulted in a microstructure with a less distinct pattern than in rapidly quenched specimens.

Vogel recognised that annealing at high temperatures could produce a microstructure with two phases of different phosphorus content and that this inhomogeneity of phosphorus was maintained when a rapid quench was applied. The nital etch displayed this inhomogeneity and, in so doing, revealed the positions of the phase boundaries between the ferrite and austenite at the annealing temperature. Slower cooling resulted in some dispersion of the

phosphorus segregation so that the prior phase boundaries were not etched sharply.

A more comprehensive study was carried out by Rocquet and Jegaden.⁷ They carried out a series of metallographic investigations of steel specimens taken during dephosphorisation of steel in a converter and of specially prepared iron-phosphorus alloys. Specimens for metallographic inspection were prepared by rapidly quenching specimens which had been annealed at high temperatures. Nital etching revealed microstructures similar to those found by both Haughton and Vogel with evidence of there having been two phases present at a range of high temperatures. Rocquet and Jegaden demonstrated that the boundaries revealed by nital corresponded to sharp changes in phosphorus concentration, which was shown by subsequent etching of the same specimens with nital and Oberhoffer's reagent. They realised that the microstructure was fully ferritic at room temperature. Any austenite present at high temperatures transformed to ferrite on quenching and the prior phase boundaries were visible because the phosphorus inhomogeneity had not been dispersed during cooling.

In their work, no clear metallographic evidence of a two phase regime was obtained in alloys of phosphorus contents less than 0.1 wt-%, although no such difficulty was encountered in those with higher phosphorus levels. Austenite tended to nucleate along grain boundaries and sometimes had an acicular morphology. Specimens were annealed in the dual phase range by heating them directly from the ferritic state and also by allowing specimens which had been fully austenitised to cool down to an appropriate temperature. Comparison of these specimens showed that the growth of ferrite from an austenitic matrix was slower than the growth of austenite from a ferritic matrix. Rocquet and Jegaden also found that the homogeneity of an iron-phosphorus alloy, which had been annealed at a temperature such that it was fully austenitic, could be maintained by a rapid quench to ambient temperatures.

Very little work has been carried out with iron-phosphorus binary alloys to investigate the microstructures that can be formed after heating in the dual phase region. The previous work was carried out primarily to try to establish the limits of the austenite and dual phase fields of the iron-phosphorus phase diagram. Many of the microstructural details described above are interpretations drawn out by the present authors and do not reflect the focus of previous work.

Austenite-ferrite transformation in ferrous systems

The Dubé classification system was devised to describe the morphologies of proeutectoid ferrite formed in carbon steels.¹¹ The morphology of the ferrite varies with the temperature of transformation. At high transformation temperatures, ferrite allotriomorphs grow by a reconstructive transformation. At larger undercoolings, growth of Widmanstätten side plates becomes possible. Widmanstätten ferrite can grow at undercoolings which are not large enough to permit diffusionless transformation. Carbon diffuses during growth but no partitioning of substitutional solutes is observed.¹² At still lower temperatures, diffusionless transformation becomes thermodynamically feasible and displacive transformations to bainite and martensite dominate.

Ferrite-austenite transformation in ferrous systems

GROWTH OF AUSTENITE FROM α -FERRITE

Most of the previous work carried out on the austenitisation of ferrous systems has concentrated on steels containing an

appreciable amount of carbon in the microstructure so that austenitisation began at former carbides and pearlite colonies¹³ and an analysis of the morphology of the austenite as it forms is of little value. Law¹⁴ investigated the austenitisation of an Fe-0.2C-1V alloy (all compositions in this paper are given in wt-% unless otherwise stated), which contained a dispersion of carbides, and only noted the growth of austenite allotriomorphs and idiomorphs.

Fong and Glover¹⁵ nitrided an Fe-1.93Mn alloy at 645°C to effect austenitisation and observed the growth of Widmanstätten side plates as well as idiomorphs and allotriomorphs. This transformation occurred isothermally and was driven by a change in the overall composition of the specimen.

Allen and Earley¹⁶ investigated the ferrite-austenite transformation in a series of iron-nickel alloys and showed the duplex microstructures produced by heating Fe-2.5 at.-%Ni and Fe-4.9 at.-%Ni alloys into the dual phase region and transforming them isothermally. Allotriomorphs, sawteeth, primary Widmanstätten plates, and idiomorphs can be identified in their photomicrographs.

GROWTH OF AUSTENITE FROM HIGH TEMPERATURE FERRITE

In a metallographic examination to determine the gamma loop in the iron-aluminium system, Rocquet *et al.*¹⁷ heated specimens of iron-aluminium alloys to 1400°C for 2 h and allowed them to cool slowly to a temperature in the dual phase region. The specimens were held at this temperature for 2-3 h and then quenched. Metallographic examination showed that the morphology of the austenite formed could be described by the Dubé classification system. Sykes¹⁸ carried out a similar metallographic investigation of the iron-tungsten gamma loop. He showed that the austenite formed by cooling high temperature ferrite into the dual phase region could have a lath morphology. In both instances, etching revealed the solute inhomogeneity remaining from high temperatures. At room temperature, the structure was entirely ferritic but the prior phases could be discerned by the differential attack of the etch.

Dual phase stainless steels have been the subject of much study. They consist of δ -ferrite at high temperatures but austenite nucleates on cooling and grows in the ferritic matrix. The mixed austenite-ferrite microstructure produced may be retained to room temperature. The morphologies of austenite produced can be classified according to the Dubé system. Similar microstructures resulting from the precipitation and growth of austenite in a ferrite matrix can be produced by quenching a stainless steel from the high temperature ferrite region to room temperature and then reheating it into the dual phase region.¹⁹⁻²⁵

Both austenite allotriomorphs and Widmanstätten side plates are commonly observed. These side plates produce a corresponding surface relief²⁵ and ledges have been observed at the austenite-ferrite interface.²⁴ It has been shown that partitioning of nickel and chromium, substitutional solutes, occurs between the growing plates of austenite and the ferrite matrix.^{21,22,24,25} Once formed, the austenite is observed to competitively coarsen.²⁴

Experimental

This study was carried out in three major sections. In the first two parts, the metallography of the phase transformations in iron-phosphorus alloys was studied. The ferrite-austenite transformation was examined in the first section and the reverse reaction, the growth of ferrite from an austenitic matrix, was studied in the second. In the final part, the ghosting patterns produced by the action of nital on these microstructures were investigated. The compos-

itions of specially prepared iron-phosphorus alloys used in this research are listed in Table 1.

FERRITE-AUSTENITE TRANSFORMATION

To study the ferrite-austenite transformation, specimens ($\sim 12 \times 5 \times 2$ mm) of homogenised iron-phosphorus alloys were sealed in silica tubes under argon (150 mmHg) and placed in preheated furnaces. The development of the dual phase microstructures in Fe-0.10P and in Fe-0.38P were investigated at 935 and 1035°C respectively. Specimens of Fe-0.20P were heat treated at 951, 972, and 991°C to show how the morphologies developed varied with the driving force for the reaction. In a preliminary study, specimens of Fe-0.20P were heated at 1150°C for 1 h and furnace cooled, air cooled, or water quenched. Examination with Oberhoffer's reagent did not reveal any segregation of phosphorus, confirming that transformation on cooling does not produce any segregation in itself. Specimens were investigated using optical microscopy with Oberhoffer's reagent, whose effectiveness in revealing microstructural segregation of phosphorus in iron has been demonstrated previously.²⁶ This reagent precipitates copper on the surface of iron. Copper is deposited preferentially on areas of lower phosphorus content so that, after etching, regions relatively low in phosphorus appear dark and those higher in phosphorus appear light.

Two specimens were examined further using a Cameca SX50 with a wavelength dispersive X-ray analysis link. Two methods of analysis were carried out. The phosphorus compositions at evenly spaced points were measured. Also, an elemental map of 128×128 points, spaced by 2 μm , was created for each specimen by measuring the phosphorus K_{α} count at each point for one second.⁴

AUSTENITE-FERRITE TRANSFORMATION

The austenite-ferrite transformation was investigated for the Fe-0.20P alloy only. Cylinders of the homogenised alloy (~ 10 mm diameter and ~ 90 mm length) were heated in a Gleeble 1500 thermomechanical tester. Around 20 mm length at each end of the bar was clamped between sets of water cooled copper jaws. The temperature was measured by a chromel/alumel thermocouple spot welded halfway along the length of the bar. The specimen was given the following heat treatment: 1 min at 900°C to allow temperature control adjustment and stabilisation, 10 min at 1100°C to effect complete austenitisation, and various times at 940°C to permit the initial growth of ferrite with partitioning of phosphorus. Rapid heating and cooling rates ($\sim 15^{\circ}\text{C s}^{-1}$) between the individual isothermal stages were employed. Specimens were austenitised and heated at 940°C for 30 min, 1 h, and 4 h. Longer heat treatments were not practical using the Gleeble.

Temperatures at the bottom of the dual phase region were investigated in order to see if acicular ferrite morphologies would be produced if the transformation was carried out with as high a driving force as possible. During preliminary experiments, it was found that at temperatures down to $\sim 940^{\circ}\text{C}$, a clear microsegregation of phosphorus could be detected using Oberhoffer's reagent. At lower temperatures, no clear evidence of partitioning of phosphorus was observed after transformation to ferrite. Some

boundaries in the specimen could be detected but these were not accompanied by a significant variation in phosphorus content. Below about 940°C, it is to be expected that the massive austenite-ferrite transformation from, which occurs without partitioning of phosphorus, dominates, as described by Shewmon.⁸

METALLOGRAPHY WITH NITAL AS ETCH

Iron-phosphorus specimens, which had been heat treated in the dual phase region to produce an uneven phosphorus content, were etched with nital and examined optically using bright field illumination and differential interference contrast (Normaski). In particular, one specimen of Fe-0.20P alloy, heated at 972°C for 24 h and water quenched, was examined. After polishing to a mirror finish, a microhardness indent was placed on the surface of the specimen. This mark on the surface allowed easy re-identification of a specific region. Profilometry was also used to investigate the surface of metallographic specimens after etching with nital.

To investigate homogenisation after microsegregation at elevated temperatures, specimens were cut from a block of Fe-0.20P alloy that had been heated at 972°C for 24 h and water quenched to produce an uneven distribution of phosphorus. The specimens were then heated at 800 or 900°C to initiate homogenisation of the alloy and were subsequently investigated metallographically after etching with nital.

Results and discussion

FERRITE-AUSTENITE TRANSFORMATION

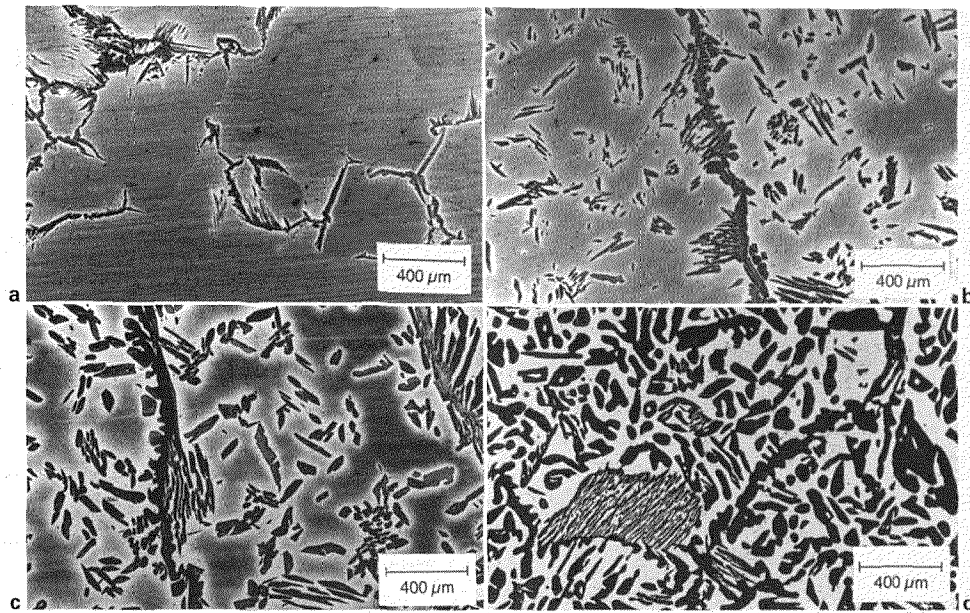
Figure 3 shows the development of the dual phase microstructure in Fe-0.20P specimens heated at 972°C. Figure 4 shows prior austenite nucleates with an acicular morphology, growing from a grain boundary. The isolated blocks of prior austenite beyond the tips of the fingers of austenite suggest that these features are needles rather than plates, the isolated blocks being sections of these needles in the plane of examination. Initially, austenite nucleated and grew from the ferrite grain boundaries as allotriomorphs and needles and then became more developed while intragranular precipitation was also observed at longer times. After 24 h, a dual phase microstructure had developed fully. There is no evidence of a phosphorus concentration gradient in the ferrite, suggesting that the system had approached equilibrium. The austenite had begun to spheroidise and competitively coarsen.

Close inspection of these microstructures further demonstrates the ability of Oberhoffer's reagent to reveal microstructural variations in phosphorus content. The initial austenite form appeared to be slightly lower in phosphorus (darker) than the matrix. The ferrite areas around the prior austenite appeared lighter, indicating that these regions were locally higher in phosphorus, thus revealing a concentration gradient of phosphorus in the ferrite matrix. Phosphorus had been expelled from the regions that had transformed to austenite and diffused into the bulk ferrite. At longer heating times, the light 'halo' of high phosphorus iron becomes broader, revealing a thickening of the high phosphorus band. After 24 h, two distinct contrasts are produced by Oberhoffer's reagent with no significant gradation within each, showing that an equilibrium dual phase microstructure had developed.

Similar prior phase microstructures were revealed in Fe-0.20P specimens heated at 951 and 991°C as shown in Fig. 5. However, the morphology of the austenite varied with the temperature of transformation. At 951°C dark (low phosphorus) prior austenite can be seen in a light (high phosphorus) ferrite matrix (see Fig. 5a). The austenite

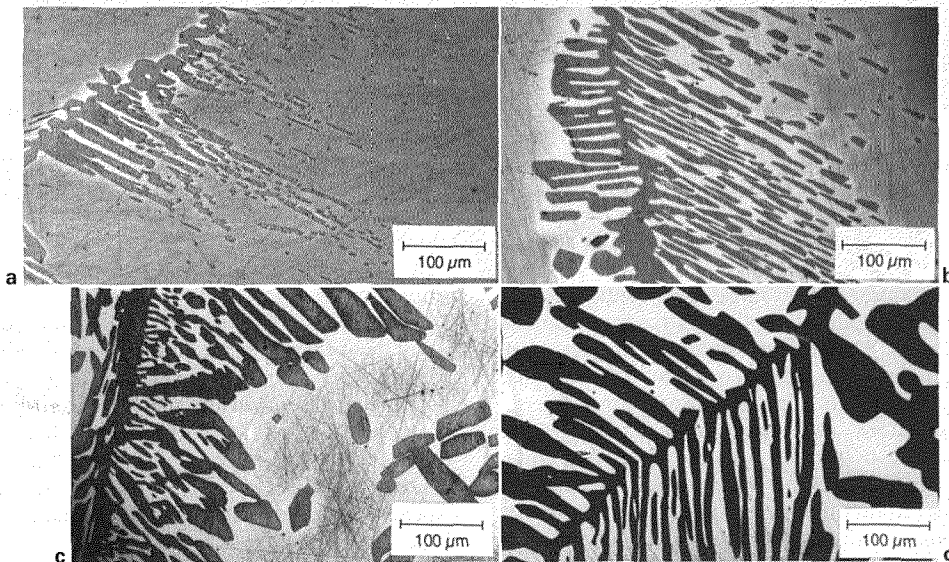
Table 1 Compositions of iron-phosphorus alloys (all homogenised prior to use⁴)

Alloy	Solute composition, wt-%						
	C	Si	Mn	P	S	Sn	Ti
Fe-0.10P	0.013	0.02	...	0.10	0.004	0.002	0.001
Fe-0.20P	0.004	0.02	...	0.20	0.004	0.002	0.001
Fe-0.38P	0.010	0.02	0.01	0.38	0.003	0.002	0.001



a 15 min; b 1 h; c 4 h; d 24 h

3 Microstructures of Fe-0.20P alloy heated at 972°C for given time, water quenched, and etched with Oberhoffer's reagent



a 15 min; b 1 h; c 4 h; d 24 h

4 Details from microstructures of Fe-0.20P alloy heated at 972°C for given time, water quenched showing prior austenite side plates, and etched with Oberhoffer's reagent

had mostly formed as allotriomorphs, but sawteeth and idiomorphs were also visible. Side plates of prior austenite were very rare.

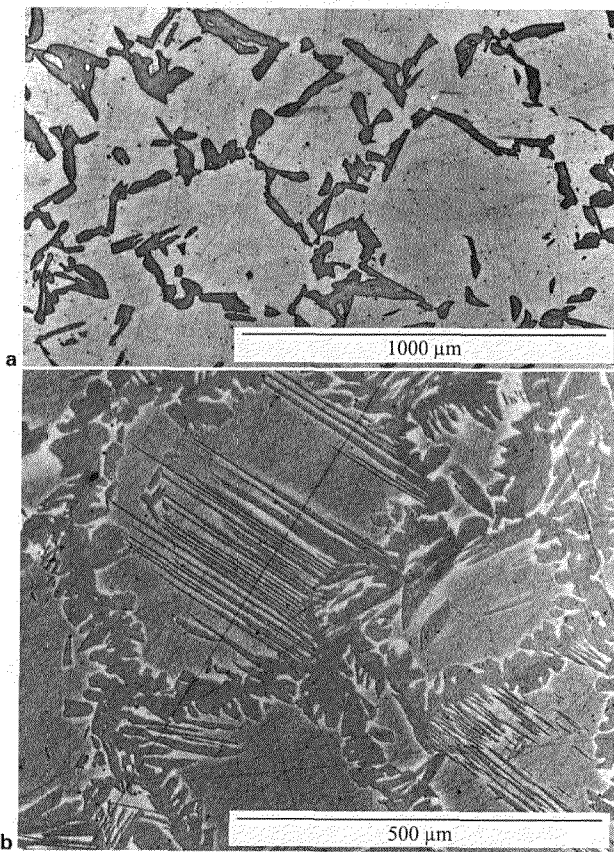
Thick allotriomorphs with spheroidised protuberances were observed in the specimen heated at 991°C (see Fig. 5b). Colonies of closely spaced secondary side plates with high aspect ratios had grown across the grain interiors. As compared to the specimen heated at 951°C, the prior austenite etched only slightly darker than the prior ferrite matrix. The local phosphorus enrichment in the ferrite at the prior phase boundary was again revealed by a light halo around the former precipitates after etching.

The reason why the matrix showed a different etched contrast in the two specimens can be explained by looking at the schematic phase diagram in Fig. 6. Horizontal tie lines, displaying the equilibrium concentrations of the prior austenite and ferrite at the former interphase boundaries, show that at 991°C the concentration of the prior austenite is closer to that of the original prior ferrite matrix than

at 951°C. Thus, the differential response achieved with Oberhoffer's reagent in the two specimens can be explained in terms of the phosphorus distribution. At 951°C, the precipitates are markedly lower in phosphorus than the matrix and so the prior austenite etches dark in a light matrix. At 991°C, the precipitates have a similar phosphorus content to the matrix, and thus both etch dark while the high phosphorus regions of expelled solute etch light.

The formation of austenite plates is favoured by higher temperatures, as can be seen in Fig. 5b, when the degree of superheating, and hence the driving force for transformation, is greater. Calculated values of the free energies of transformation from ferrite to austenite are given in Table 2 and confirm that the driving force increases with temperature.

It was observed that, at higher temperatures, the aspect ratio of the plates was higher. This can be explained in terms of constraint by the strain field of the matrix. Higher



a 951°C for 4 h; b 991°C for 15 min and water quenched

5 Prior phase microstructures of Fe-0.20P alloy heated under given conditions, etched with Oberhoffer's reagent

driving forces for transformation more easily outweigh the volume strain energy produced in the matrix by advancement of the needle tip. Also, it is possible that an increased driving force might promote ledge growth by reducing any activation energy barriers to ledge formation or movement.

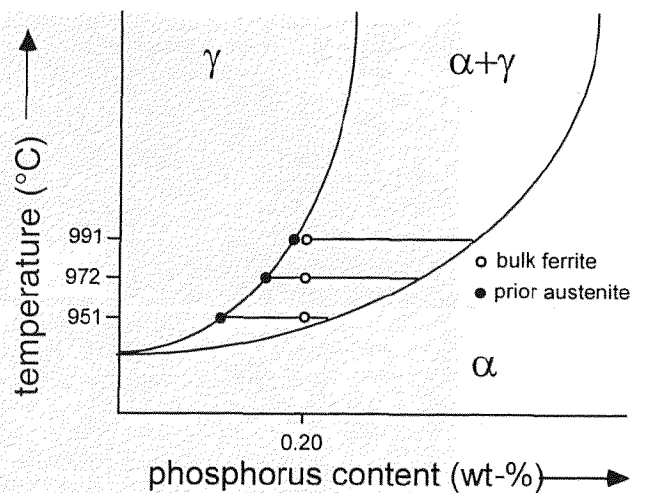
Similar microstructural developments were observed in the Fe-0.10P and Fe-0.38P alloys (see Fig. 7). Austenite formed in both alloys by a diffusion controlled nucleation and growth process so that the proportion of prior austenite (dark) visible upon metallographic examination increased as the length of the heat treatment increased. Prolonged heating produced competitive coarsening and spheroidisation of the two phases as equilibrium was approached, as for the Fe-0.20P alloy.

The prior phases etched most clearly in the Fe-0.38P alloy, presumably because of a larger variation in phosphorus composition. Accordingly, the prior phases etched least clearly in the Fe-0.10P alloy, although they were still identifiable.

Table 2 Calculations of free energies of ferrite-austenite transformation for Fe-0.20P-0.02Si-0.004S-0.0004B-0.002Sn using MTDATA*

Temperature, °C	Free energy of ferrite-austenite transformation $\Delta G_{\alpha-\gamma}$, kJ mol ⁻¹
951	-2.4
972	-23.2
991	-38.9

* Computer package MTDATA (National Physical Laboratory, Teddington, Middx TW11 0LW) provides and uses thermodynamic phase data to calculate free energies of phases in multicomponent alloys.⁴



6 Schematic diagram illustrating gamma loop of iron-phosphorus phase diagram with tielines for the temperatures investigated

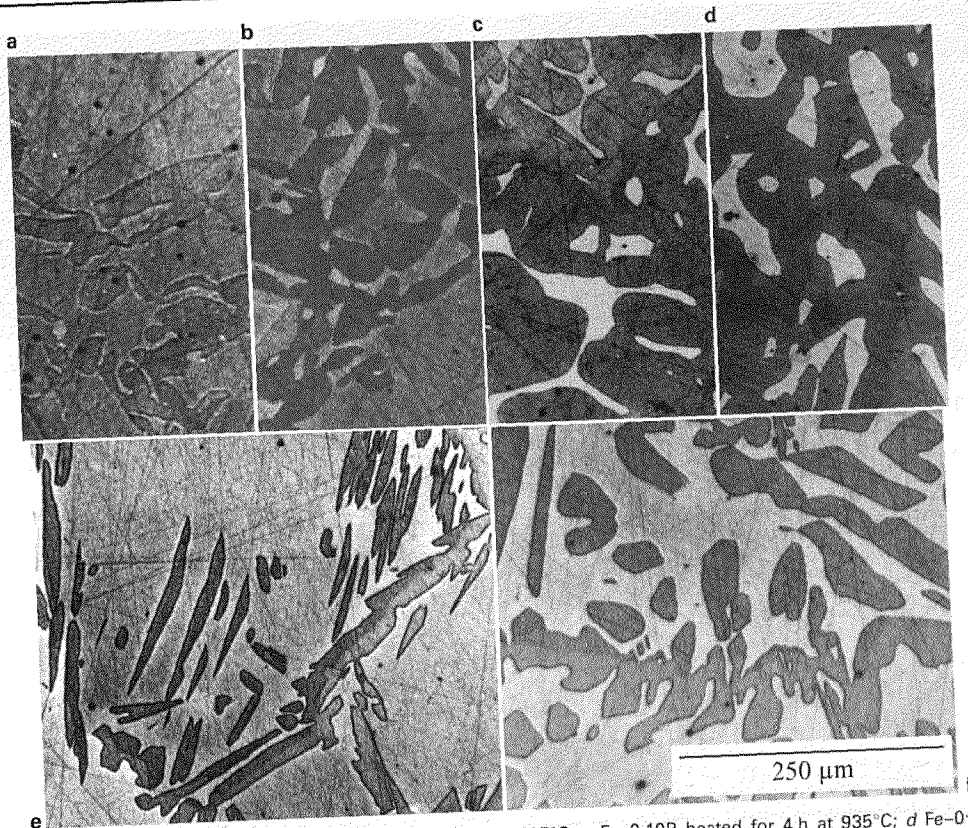
Two specimens previously examined metallographically were investigated using WDX analysis, the Fe-0.38P alloy specimens heated at 1035°C for 15 min and for 1 h. Metallographic examination of the specimen heated for 1 h clearly showed the two prior phases of ferrite and austenite (see Fig. 8a). The two prior phases etched light and dark respectively with no apparent gradation in contrast within either, implying that the phosphorus contents were approximately constant within each phase. The boundaries between the prior phases were smooth and curved and showed that some spheroidisation of the prior phases had occurred. These observations suggested that the system had approached equilibrium.

In the specimen heated for 15 min however, a smaller proportion of prior austenite (darker) was visible demonstrating that the transformation had not progressed as far as in the other specimen (see Fig. 9a). Sharp needles of prior austenite could be seen. The prior austenite etched homogeneously dark but the ferrite immediately adjacent to the prior austenite etched lighter than the bulk ferrite. This indicated a build-up of phosphorus ahead of the advancing austenite-ferrite interface as the phosphorus, expelled from the austenite, had not had sufficient time to diffuse into the bulk.

Figures 8b and 9b show the phosphorus composition measured along lines between the vertices of indentations on the specimens' surfaces with the corresponding images obtained by etching with Oberhoffer's reagent aligned below. Figure 10 displays the X-ray maps of phosphorus distribution together with the corresponding optical micrographs. There is a direct correspondence between the results of optical microscopy with Oberhoffer's reagent and X-ray analysis, confirming the ability of this etch to reveal variations in phosphorus content.

From close inspection of the WDX results, it appeared that equilibrium conditions were maintained at the interface and that the growth of austenite was limited by the diffusion of phosphorus into the bulk ferrite.⁴ Thickening of the austenite, therefore, would be expected to increase the width of the solute diffusion profile in the ferrite as solute must be preserved. This broadening of the solute diffusion profile was observed optically with Oberhoffer's reagent.

Studies reported elsewhere by Stewart⁴ also demonstrated how the phosphorus inhomogeneity could be gradually dispersed by heating specimens in the fully ferritic regime at 800 and 900°C, and also suggested that growth of austenite laths produces a surface relief.



a Fe-0.10P heated for 15 min at 935°C; b Fe-0.10P heated for 1 h at 935°C; c Fe-0.10P heated for 4 h at 935°C; d Fe-0.10P, 24 h at 935°C; e Fe-0.38P heated for 15 min at 1035°C; f Fe-0.38P heated for 1 h at 1035°C

7 Microstructures of iron-phosphorus alloys heated into the dual phase range, water quenched, and etched with Oberhoffer's reagent

AUSTENITE-FERRITE TRANSFORMATION

Etching the heat treated Fe-0.20P specimens with Oberhoffer's reagent revealed the phosphorus inhomogeneity remaining from the growth of ferrite in the austenite matrix at 940°C. Regions which had transformed to ferrite at elevated temperature had a higher phosphorus content and so etched lighter than the matrix. The iron immediately adjacent to that which had transformed at 940°C etched dark, suggesting that the surrounding austenite had been depleted of phosphorus.

As the time of heating at 940°C was increased, the proportion of prior ferrite visible in the microstructure increased. The high phosphorus ferrite nucleated and grew as irregular bands, probably allotriomorphs along prior austenite grain boundaries. Figure 11 shows that at longer heat treatments, these allotriomorphs were thicker and had joined up to form a continuous network. Oberhoffer's reagent also showed a slight response to grain orientation as has been observed previously.²⁶

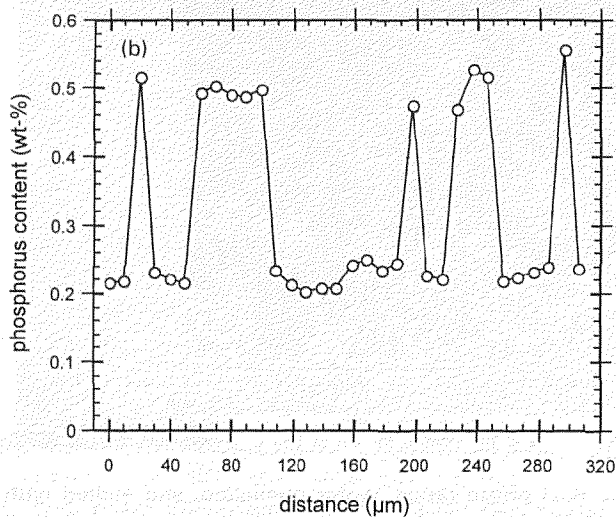
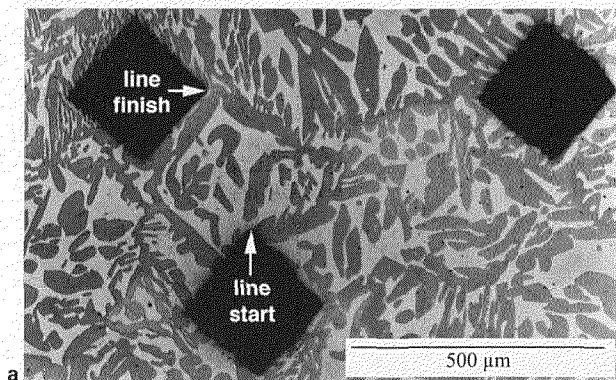
Numerous sawteeth could be seen (see Fig. 12a). These appeared to grow from the sites of former austenite grain boundaries, as indicated by the allotriomorphs. Occasionally, a few side plates could be seen (see Fig. 12b). These had too high an aspect ratio to be classifiable as simple sawteeth. Where more than one plate was seen, they usually lay parallel to one another suggesting a crystallographic relationship with the matrix, as would be expected. A few plates showed ledge structures of the order of 4 μm high on one of their faces (see Fig. 12c). These are possibly 'superledges' created by the accumulation of individual growth ledges.²⁷

Ferrite plates were considerably rarer than sawteeth. The specimen heated at 940°C for 4 h showed acicular morphologies of the prior ferrite more frequently and intragranular needles could be seen. Figure 12d shows two variants of needles together. On close inspection, it appears that one

needle has nucleated at and grown from the surface of another. This event, which was noted at several other points in the microstructures examined, is referred to as 'sympathetic nucleation'.²⁸ Many of the needles and plates did not have sharp tips but were rounded or slightly blocky in appearance. This is probably due to some spheroidisation driven by a net reduction in interfacial area. This effect was not noted in the very early stages of the formation of austenite in a ferrite matrix. The rate of spheroidisation depends upon the structure of the interface and so is likely to be similar for the ferrite-austenite as for the austenite-ferrite transformation. However, as the austenite-ferrite transformation is relatively slower due to a lower diffusivity of phosphorus in the matrix, the effects of spheroidisation can be observed when transformation is still far from complete.

Two parallel side plates of ferrite, observed in the Fe-0.20P specimen austenitised and transformed at 940°C, were analysed using the Cameca SX50 with the wavelength dispersive detector. Phosphorus concentrations were measured at points along two lines, one crossing the side plates, the other along the length of one plate. Figure 13a shows the area analysed etched with Oberhoffer's reagent. Figure 13b shows the surface of the specimen after repolishing and X-ray analysis. Points where analyses were made have been discoloured due to the electron beam having been focused at these locations. This allowed the points analysed to be related exactly to the microstructure as revealed by Oberhoffer's reagent. This method of identifying linescans had not been possible in the previous WDX analysis of prior austenite in a ferrite matrix as the information had been obscured during scanning of the entire region with the electron beam to produce maps of elemental distribution.

From comparison of the photomicrographs, it can be stated that the line AB crossed prior ferrite side plates

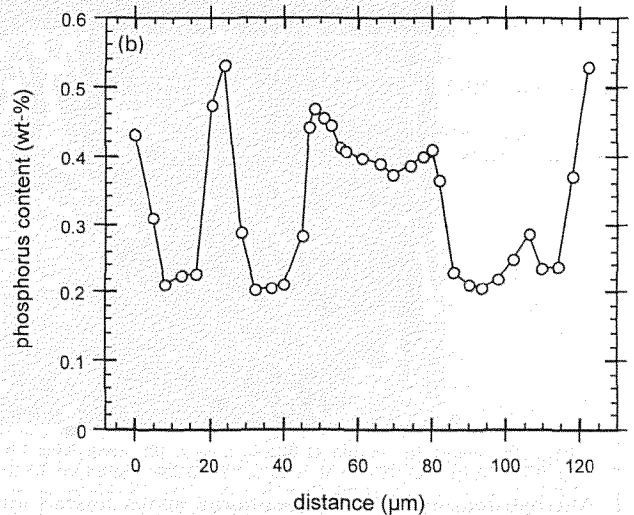
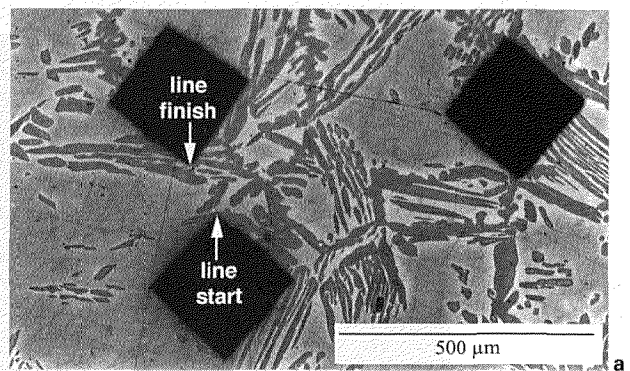


8 Specimen of Fe-0.38P heated for 1 h at 1035°C, water quenched, and etched with Oberhoffer's reagent a region analysed by WDX: dark square regions are Vickers hardness indents; pictures under graphs are sections of microstructure along which the lines of points were traced, as revealed by Oberhoffer's reagent b phosphorus composition measured along a line using WDX analysis: map of phosphorus content 256 μm wide; optical photographs are to same scale within error of $\pm 2\%$

19–23 and 46–49 μm from the starting point A. On the longitudinal scan of the side plate CD, the tip of the prior ferrite plate lay 25 μm from the starting point C. About 16 μm from point C, the beam was measuring points close to the edge of the plate which explains why the measured values were lower than those expected if the entire volume being sampled had been prior ferrite. The direct correspondence between the results of optical microscopy and X-ray analysis again confirms the ability of Oberhoffer's reagent to reveal phosphorus microsegregation.

The lateral scan showed the characteristic diffusion profile of the depletion layer in the prior austenite at the prior austenite-ferrite boundary. Solute was being removed from the austenite at the phase interface, setting up a concentration gradient within the austenite matrix. Phosphorus from the bulk diffused down this gradient towards the interface. The longitudinal scan did not reveal any broad layer depleted in phosphorus ahead of the advancing tip. As the tip advanced, this diffusion profile would have been maintained due to a point effect of geometry so that the lengthwise growth rate of the plate did not diminish with time.^{29,30}

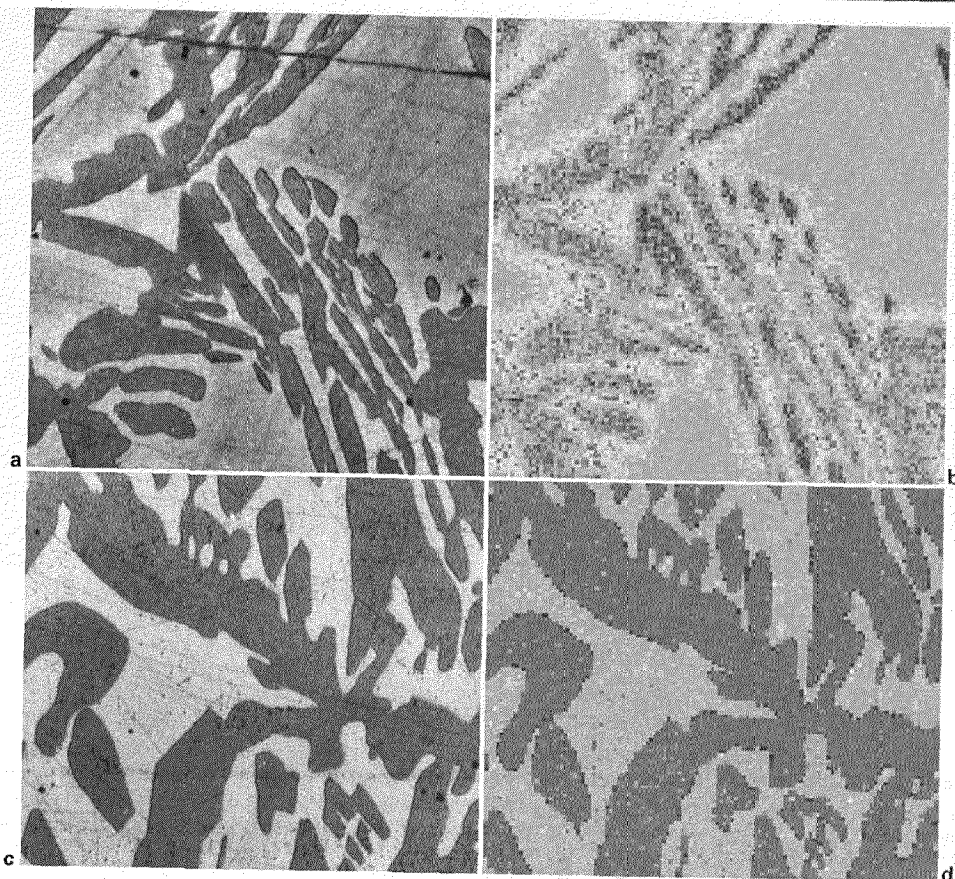
The morphologies of ferrite formed at 940°C can be described by the Dubé classification system.^{11,28,31} Three differences between the plates of ferrite observed in this study and the Widmanstätten plates commonly observed



9 Specimen of Fe-0.38P heated for 15 min at 1035°C, and water quenched, a region analysed by WDX analysis: dark square regions are Vickers hardness indents; pictures under graphs are sections of microstructure along which the lines of points were traced, as revealed by Oberhoffer's reagent b phosphorus compositions measured along a line using WDX analysis: map of phosphorus content 256 μm wide; optical photographs are to same scale within error of $\pm 2\%$

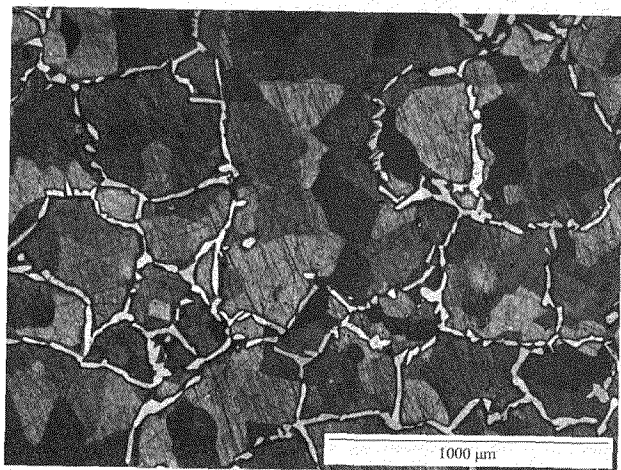
in carbon steels were noted. First, the growth of the ferrite plates was accompanied by the partitioning of phosphorus, even though it is a substitutional solute, whereas during the growth of Widmanstätten plates in a conventional steel, it is generally accepted that carbon is partitioned between the ferrite and the austenitic matrix and no partitioning of substitutional solutes occurs.^{12,32–34} Hence these ferritic plates must have grown by a wholly reconstructive transformation. Second, Widmanstätten ferrite plates in a conventional steel are found to remain perfect in shape with prolonged holding at temperature²⁸ whereas the ferrite needles observed in the phosphoric iron spheroidise. This may be at least partly due to the very different transformation temperatures in these two instances. Third, in all the microstructures observed, the prior ferrite rarely displayed an acicular morphology. Side plates and intragranular plates appeared to be more common at longer times of transformation.

The thermodynamic computer package MTDATA was used to calculate the free energy change upon complete transformation from austenite to ferrite for an Fe-0.30C steel at 650°C (-288 kJ mol^{-1}) and for the alloy under investigation at 940°C (-10 kJ mol^{-1}). It can be seen that the driving force for transformation of the phosphoric iron is considerably less than that of the steel at a temperature at which Widmanstätten ferrite would commonly be produced. The driving force for transformation in the



a optical micrograph of specimen heated at 1035°C for 15 min (etched with Oberhoffer's reagent); b X-ray map of phosphorus composition of same area as a (lighter regions are higher in phosphorus); c optical micrograph of specimen heated at 1035°C for 1 h (etched with Oberhoffer's reagent); d X-ray map of phosphorus composition of same area as c

10 Regions on Fe-0.38P specimens mapped using WDX analysis for phosphorus content: maps of phosphorus content 256 μm wide; optical micrographs to same scale within error $\pm 2\%$



11 Microstructure of Fe-0.20P alloy which has been austenitised at 1100°C for 10 min, then transformed at 940°C for 4 h, and etched with Oberhoffer's reagent: light areas of higher phosphorus prior ferrite had transformed at 940°C; etch has also revealed grain structure by etching each grain slightly different contrast

phosphoric iron is increased by lowering the temperature. In practice it was found that lowering the transformation temperature did not promote the formation of plates of ferrite as the massive reaction was so encouraged that it dominated.

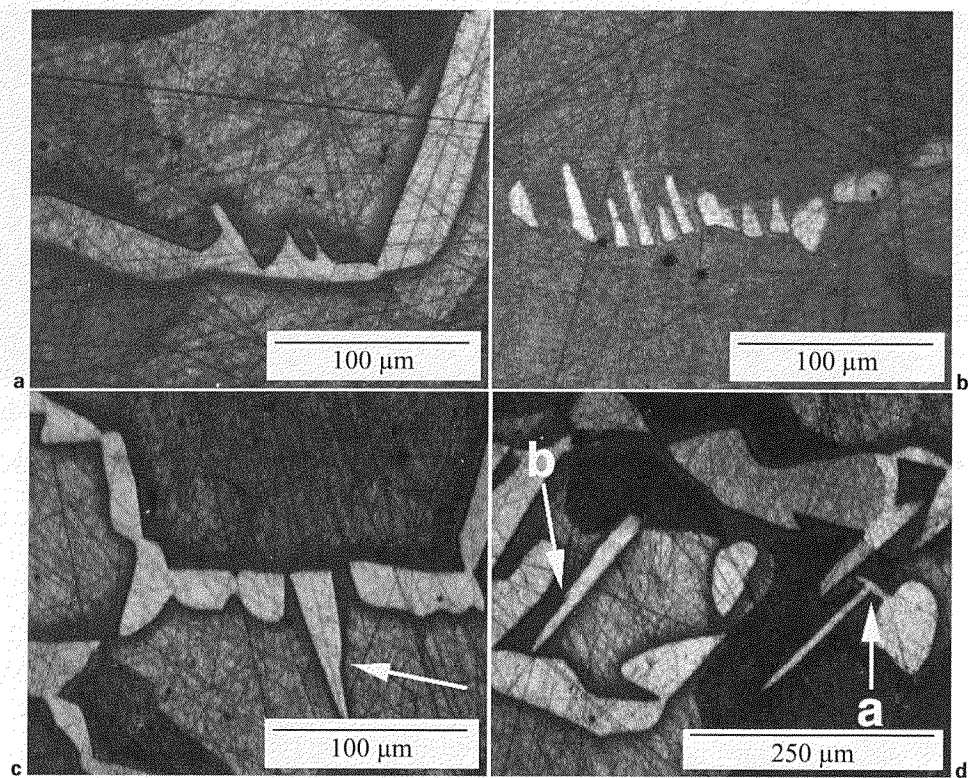
METALLOGRAPHY WITH NITAL AS ETCH

Etching the specimens with nital produced ghostlines (see Fig. 14). These corresponded to the boundaries between

high and low phosphorus regions revealed by Oberhoffer's reagent. This confirmed previous results which showed that the ghostlines were associated with a sudden change in phosphorus content.⁷ The ghostlines could be seen clearly as the microscope was moved into and out of focus. As the microscope was adjusted to the other side of focus, the phase which had previously appeared slightly darker now appeared lighter (cf. Fig. 14a and b). Differential contrast indicated that the ghostlines corresponded to a sharp change in surface relief.⁴ When tilted, the side of the specimen which was tilted upwards remained bright while the other appeared dark (see Fig. 14c). The direction of tilting was confirmed by reflection from the surface upheavals surrounding the microhardness indent. The prior austenite and ferrite phases were clearly visible. It could be seen that the nital had attacked one of the prior phases preferentially. Repolishing and etching with Oberhoffer's reagent (see Fig. 14d) showed that the nital had attacked the low-phosphorus prior austenite region preferentially. Subsequent experiments using profilometry confirmed this result.⁴

Nital produced ghosting patterns in the specimens with partially dispersed prior dual phase phosphorus distributions which were given short heat treatments. No ghosting was produced in those given the longest heat treatments (see Fig. 15). This confirms that ghosting patterns are the product of local gradients in phosphorus. The ghosting becomes indistinct as the phosphorus content gradient decreases and finally disappears as the alloy is homogenised. The microstructures are described in Table 3.

Comparison of the specimens heated at 800 and 900°C showed that those which had been given a heat treatment which allowed a comparable amount of phosphorus diffusion in the fully ferritic region produced similar



a prior ferrite side plates growing from secondary sawteeth in specimen heated at 940°C for 4 h; b primary side plates and sawteeth in a specimen heated at 940°C for 1 h; c secondary side plate of prior ferrite sawteeth in a specimen heated at 940°C for 4 h (side plate shows an unusual ledge feature on one side marked by arrow); d prior ferrite plates showing evidence of sympathetic nucleation (point where sympathetic nucleation is believed to have occurred is indicated by arrow a), one prior ferrite plate shows unusual ledge feature on one side (arrow b)

12 Details from microstructures of Fe-0.20P specimens which were austenitised at 1100°C for 10 min and then partially transformed at 940°C before rapid cooling towards room temperature (etched with Oberhoffer's reagent)

ghosting patterns. The ghostlines become less sharp for longer diffusion distances. This corresponded to the change in phosphorus content in the underlying metal becoming gradual. Indistinct ghostlines were also produced in specimens which had been furnace cooled from the dual phase region.⁴

These results show how the ghosting effect is lost as the inhomogeneity in phosphorus content is dispersed. In the specimens heated for 4 h at 900°C and for 24 h at 800°C,

Oberhoffer's reagent could still detect a slight inhomogeneity.⁴ However, nital did not produce a noticeable ghosting effect (Fig. 15). This shows that even in the presence of an uneven phosphorus distribution, ghosting will not be observed unless the magnitude of variation in, and the gradient of, phosphorus content are both sufficiently large.

Table 3 Microstructures produced by etching specimens with nital and corresponding diffusion distances of phosphorus: estimates of diffusion distances \sqrt{Dt} were made using values of activation energy and diffusion coefficient quoted in Askill³⁵ for temperature range 700–850°C

Length of heat treatment	Microstructure as revealed by nital after heating at	
	800°C	900°C
15 min	Ghosting with distinct boundaries, ferrite grain boundaries very faintly revealed $\sqrt{Dt} = 2.1 \mu\text{m}$	Ferrite grain boundaries distinctly etched, ghosting clearly visible but boundaries not sharp $\sqrt{Dt} = 4.7 \mu\text{m}$
1 h	Ferrite grain boundaries distinctly etched, ghosting clearly visible but boundaries not sharp $\sqrt{Dt} = 4.2 \mu\text{m}$	Ferrite grain boundaries clearly etched, ghosting still visible but not distinctly defined $\sqrt{Dt} = 9.4 \mu\text{m}$
4 h	Ferrite grain boundaries clearly etched, ghosting still visible but not distinctly defined $\sqrt{Dt} = 8.5 \mu\text{m}$	Ferrite grain boundaries clearly etched, no ghosting visible $\sqrt{Dt} = 18.8 \mu\text{m}$
24 h	Ferrite grain boundaries clearly etched, no ghosting visible $\sqrt{Dt} = 20.7 \mu\text{m}$	Ferrite grain boundaries clearly etched, no ghosting visible $\sqrt{Dt} = 46.2 \mu\text{m}$

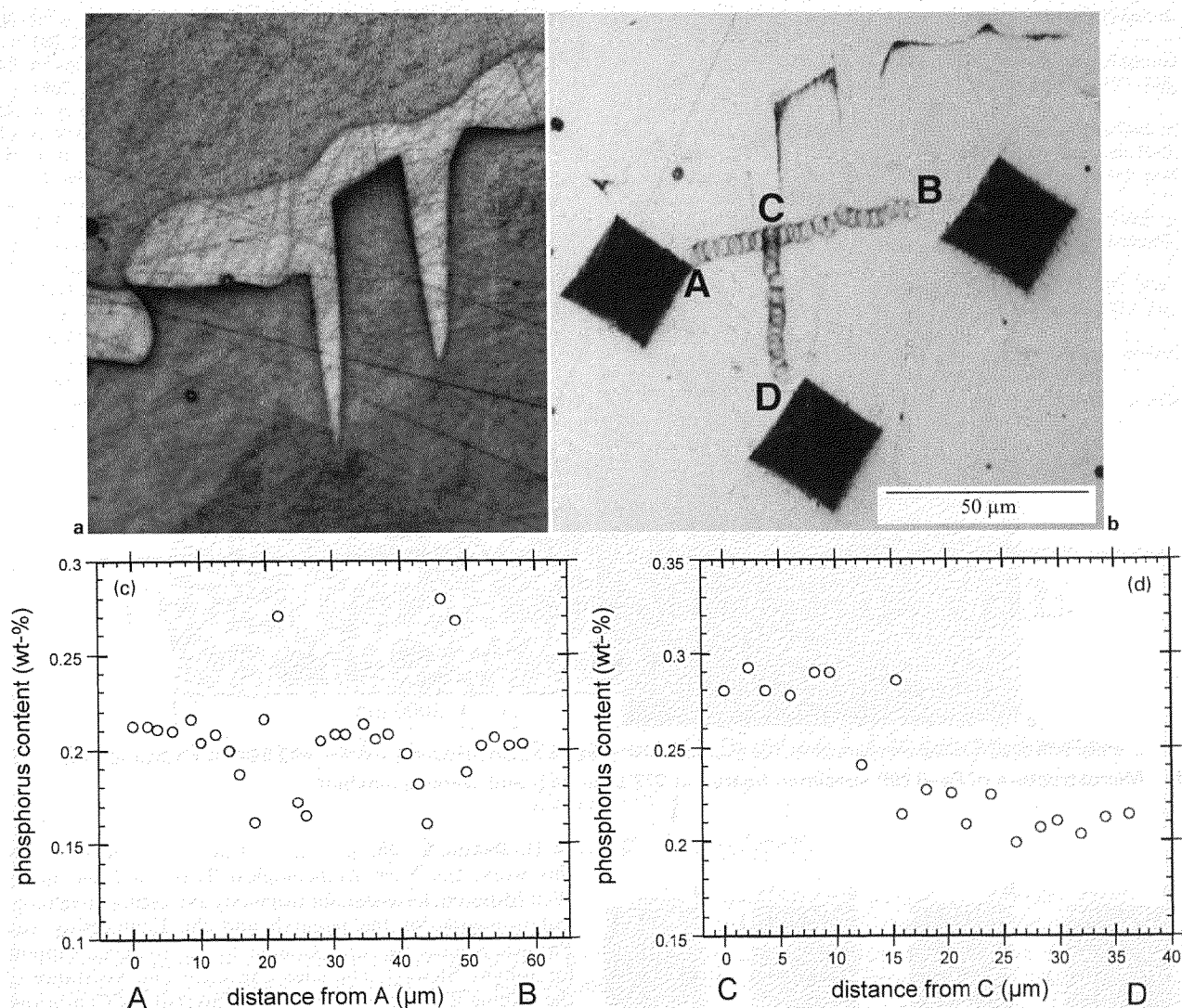
Conclusions

1. Heating a ferritic iron-phosphorus alloy into the dual phase region causes the formation of austenite by a nucleation and growth process. The morphology of the austenite can be described by the Dubé classification system. Prolonged heating causes spheroidisation and competitive coarsening of the austenite. Phosphorus is partitioned and equilibrium is maintained at the ferrite-austenite interface during the transformation. The rate of reaction is controlled by the diffusion of phosphorus in the ferrite.

2. As the driving force for transformation is increased by heating to higher temperatures, there is a greater tendency for Widmanstätten austenite to form, the spacing of the side plates decreases and their aspect ratio increases. At very low superheat, Widmanstätten austenite forms only rarely and allotriomorphs are the dominant morphological type.

3. As for the other morphologies observed, Widmanstätten austenite forms with the partitioning of phosphorus, a substitutional solute, showing that the transformation is wholly reconstructive. Circumstantial evidence was found for the production of surface relief during the growth of Widmanstätten austenite.

4. On cooling to room temperature, the austenite transforms to ferrite. Even at slow cooling rates, the



13 *a* prior ferrite side plates as revealed by Oberhoffer's reagent in an Fe-0.20P specimen austenitised at 1100°C for 10 min and transformed at 940°C for 30 min before rapid cooling towards room temperature, *b* same region as *a* after repolishing and WDX analysis, can be related to microstructure revealed by Oberhoffer's reagent as polishing did not entirely remove deep etching along edge of the allotriomorph allowing positions of side plates to be identified, *c* phosphorus compositions measured along line laterally crossing two plates of prior ferrite, line traversed is marked AB in *b*, from metallographic examination prior ferrite was crossed 19–23 μm and 46–49 μm from starting point A, and *d* phosphorus compositions measured longitudinally along plate of prior ferrite, line traversed is marked CD in *b*, from metallographic examination, tip of prior ferrite plate lay 25 μm from starting point C

phosphorus inhomogeneity of the duplex microstructure is maintained. Slow cooling or reheating in the fully ferritic domain causes diffusion of phosphorus to occur so that the discontinuity in phosphorus content at the prior phase boundaries is removed and a more gradual change in composition is observed. A very long heat treatment at a high temperature in the fully ferritic region results in homogenisation.

5. The austenite–ferrite reaction in the dual phase region is relatively slow compared with the ferrite–austenite transformation due to a lower diffusivity of phosphorus in the matrix. Due to the degree of temperature control and stability required to produce this transformation, it is unlikely that a phosphorus distribution remaining from the precipitation of ferrite in an austenite matrix would be observed in archeological phosphoric iron.

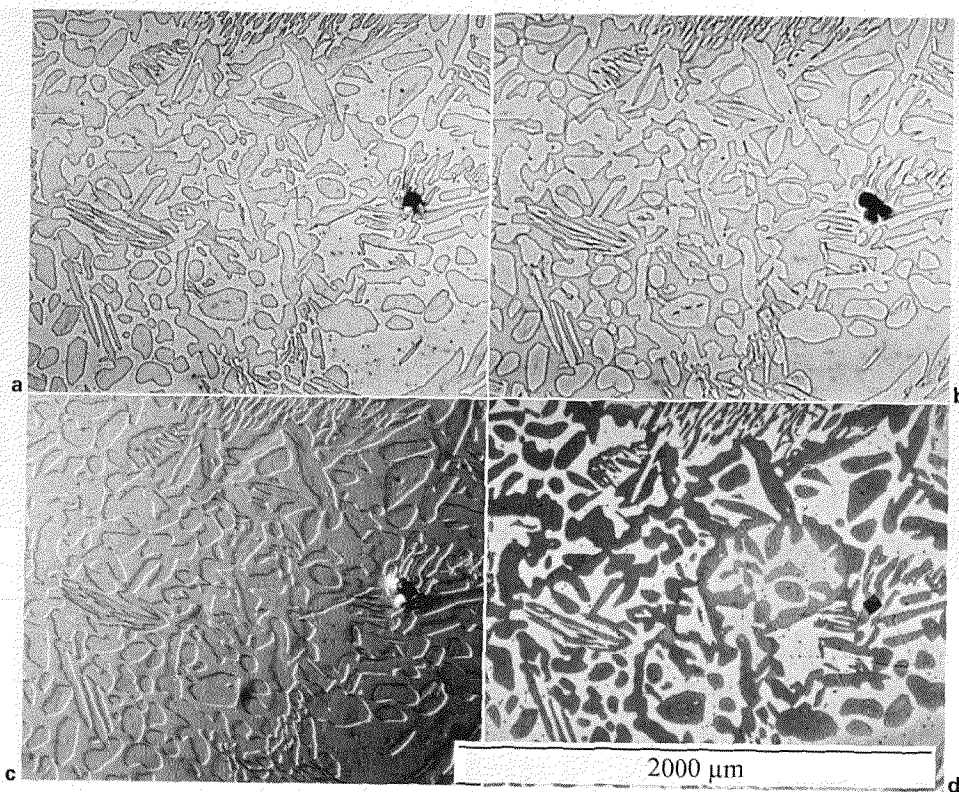
6. Ghostlines, which can sometimes be seen during the metallographic examination of high phosphorus iron, mark sharp changes in local phosphorus content in solid solution. The ghostlines are produced by the action of nital, which gives rise to a surface relief. The degree of attack produced

by the etch depends upon the local phosphorus content. The distinctness of the ghostline depends upon the local height gradient produced by the nital etch and this, in turn, depends upon the local phosphorus concentration gradient. In a microstructure with remnant phosphorus inhomogeneity reflecting a prior dual phase structure, steep concentration gradients at the prior phase boundaries etch as visible ghostlines. Ghosting will not be observed if the magnitude of variation in, or the local gradients of, phosphorus content are low.

7. The results achieved vindicated previous work²⁶ on the efficacy of Oberhoffer's reagent in qualitatively revealing variations of phosphorus content in solid solution.

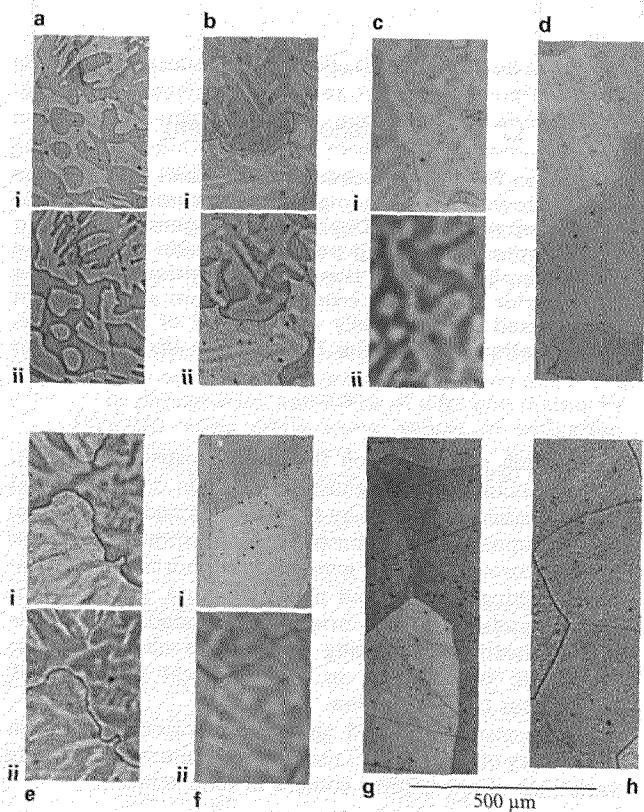
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a etched with nital; b etched with nital, other side of focus; c etched with nital, specimen tilted; d etched with Oberhoffer's reagent, bright field

14 Microstructure of Fe-0.20P specimen heated at 972°C for 24 h and water quenched



a 15 min at 800°C, i and ii on either side of focus; b 1 h at 800°C, i and ii on either side of focus; c 4 h at 800°C, i in focus, ii out of focus; d 24 h at 800°C; e 15 min at 900°C, i and ii on either side of focus; f 1 h at 900°C, i in focus; ii out of focus; g 4 h at 900°C; h 24 h at 900°C

15 Microstructures of Fe-0.20P alloy specimens heated at 972°C for 24 h, water quenched and reheated in fully ferritic region, etched with nital

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References

1. G. McDONNELL: *World Archaeol.*, 1989, **20**, 373-382.
2. K. WIEMER: 'Early British iron edged tools - a metallurgical study', PhD thesis, University of Cambridge, 1993.
3. J. E. STEAD: *J. Iron Steel Inst.*, 1915, **91**, 140-181.
4. J. STEWART: 'The metallurgy and metallography of archaeological iron', PhD thesis, University of Cambridge, 1997.
5. H. HANSEN and K. ANDERKO: 'Constitution of binary alloys'; 1973, New York, McGraw-Hill.
6. R. P. ELLIOT (ed.): 'Constitution of binary alloys - first supplement'; 1965, New York, McGraw-Hill.
7. P. ROCQUET and G. JEGADEN: *Rev. Métall.*, 1951, **48**, 712-721 and 793-810.
8. P. G. SHEWMON: 'Transformations in metals'; 1969, New York, McGraw-Hill.
9. J. L. HAUGHTON: *J. Iron Steel Inst.*, 1927, **115**, 417-433.
10. R. VOGEL: *Arch. Eisenhüttenwes.*, 1929, **3**, 369-381.
11. C. C. DUBE, H. I. AARONSON, and R. F. MEHL: *Rev. Métall.*, 1958, **55**, 201-210.
12. M. ENOMOTO: *Metall. Mater. Trans. A*, 1994, **25A**, 1947-1955.
13. L. E. SAMUELS: 'Optical microscopy of carbon steels'; 1980, Materials Park, OH, ASM International.
14. N. C. LAW: 'The austenite-ferrite transformations in low-alloy steels', PhD thesis, University of Cambridge, 1977.
15. H. S. FONG and S. G. GLOVER: *Trans. Jpn Inst. Met.*, 1975, **16**, 115-122.

16. N. P. ALLEN and C. C. EARLEY: *J. Iron Steel Inst.*, 1950, **166**, 281–288.
17. P. ROCQUET, G. JEGADEN, and J. C. PETIT: *J. Iron Steel Inst.*, 1967, **205**, 437–441.
18. W. P. SYKES: *Trans. AIME*, 1931, **95**, 301–311.
19. K. KUO: *J. Iron Steel Inst.*, 1955, **181**, 134–137.
20. H. D. SOLOMON: in 'Duplex stainless steels', (ed. R. A. Lula), 41–69; 1983, Materials Park, OH, ASM International.
21. S. ATAMERT and J. E. KING: *Acta Metall. Mater.*, 1991, **39**, 273–285.
22. S. ATAMERT and J. E. KING: *Z. Metallkd.*, 1991, **81**, 230–239.
23. S. SHARAFI: 'Microstructure of super-duplex stainless steels', PhD thesis, University of Cambridge, 1993.
24. P. D. SOUTHWICK and R. W. K. HONEYCOMBE: *Met. Sci.*, 1980, **14**, 253–261.
25. Y. OHMORI, K. NAKIA, H. OHTSUBO, and Y. ISSHIKI: *ISIJ Int.*, 1995, **35**, 969–975.
26. J. STEWART, J. A. CHARLES, and E. R. WALLACH: *Mater. Sci. Technol.*, 2000, **16**, 283–290.
27. K. R. KINSMAN, E. EICHEN, and H. I. AARONSON: *Metall. Trans. A*, 1975, **6A**, 303–317.
28. H. I. AARONSON: in 'Decomposition of austenite by diffusional processes', (ed. V. F. Zackay and H. I. Aaronson), 387–546; 1962, New York, Interscience.
29. E. A. PORTER and K. E. EASTERLING: 'Phase transformations in metals and alloys', 1st edn; 1981, London, Chapman and Hall.
30. J. W. CHRISTIAN: 'The theory of transformations in metals and alloys', 1st edn; 1965, Oxford, Pergamon.
31. R. W. K. HONEYCOMBE and H. K. D. H. BHADESHIA: 'Steels – microstructure and properties', 2nd edn; 1995, London, Edward Arnold.
32. H. K. D. H. BHADESHIA: *Mater. Sci. Technol.*, 1985, **1**, 497–504.
33. C. J. YUN, K. NAKAI, H. OHTSUBO, and Y. OHMORI: *ISIJ Int.*, 1994, **34**, 43–50.
34. Y. OHMORI, H. OHTSUBO, J. C. YUN, S. OKAGUCHI, and H. OHTANI: *Metall. Mater. Trans. A*, 1994, **25A**, 1981–1989.
35. J. ASKILL: 'Tracer diffusion data for metals, alloys and simple oxides'; 1970, New York, IFI/Plenum.

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